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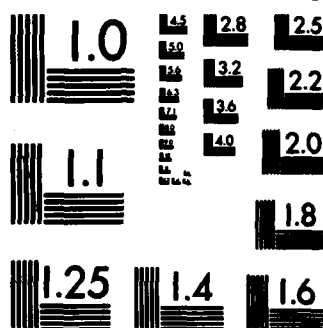
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EVIDENCE OF ELECTRONIC CONDUCTION DUE TO MIXED
OXIDATION STATES IN LUTETIUM DIPHthalOCYANINE FILMS

by

M. M. Nicholson and T. P. Weismuller

Prepared for Publication

in the

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Rockwell International Corporation
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March 1985

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<p>This note reports distinctive responses observed on reversal of the faradaic current in lutetium diphthalocyanine films which provide evidence of electronic conduction due to mixed oxidation states. Implications for reactions of the dye system at high current densities are discussed. Originator Supplied</p> <p>Key words include:</p>			
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EVIDENCE OF ELECTRONIC CONDUCTION DUE TO MIXED
OXIDATION STATES IN LUTETIUM DIPHthalOCYANINE FILMS

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This note reports distinctive responses observed on reversal of the faradaic current in lutetium diphthalocyanine films which provide evidence of electronic conduction due to mixed oxidation states. Implications for reactions of the dye system at high current densities are discussed.

Earlier papers from this laboratory described faradaic moving-boundary experiments on insulator-supported films of lutetium diphthalocyanine. With that technique, the lower end of the green dye film was immersed in a liquid electrolyte, while the upper end, several centimeters away, was connected through a metal contact to a

Key words: diphthalocyanines, electronic conduction, ion transport,
electrochromism



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constant-current power supply (1, 2). The faradaic reaction front was visible as a boundary between the colors of the reactant and product materials. Whether anodic or cathodic, this front originated at the dye/solution interface and moved upward toward the metal contact. An experimental mobility associated with the counter ion entering the film was calculated from the velocity of the boundary and the electric field in the converted film.

EXPERIMENTAL

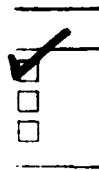
The observations reported here were made by reversal of the current in single-boundary experiments of the kind described above or in dual-boundary experiments where anodic and cathodic fronts were propagated toward one another from identical electrolyte contacts at each end of the film.

The single-boundary cells, of the type

Metal / Dye Film / Electrolyte / Counter Electrode

had the film positioned vertically and were constructed as described in Ref. 3, except that the container could be closed to maintain a controlled gas atmosphere. In the dual-boundary cells, with the configuration

Counter Electrode / Electrolyte / Dye Film / Electrolyte / Counter Electrode



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the film was positioned horizontally, and contacts to the electrolyte were made through strips of filter paper. A plastic housing was provided to control the gas atmosphere.

Lutetium dipthalocyanine test specimens were prepared by vacuum-subliming the dye onto single-crystal sapphire plates, which were heated several minutes under an infrared lamp immediately prior to the deposition stage. This procedure is thought to yield films consisting primarily of LuPc_2 .^{*} Unless the substrate is heated, however, such a film can react with air on removal from the vacuum system, possibly forming an oxygen adduct $\text{LuHPc}_2^+ \text{O}_2^-$ (4). The dye films were characterized by determining the maximum optical absorbance, at 665 nm, in the initial green state. The electrolytes were aqueous 1M Na_2SO_4 , 1M KCl , and 0.5M HCl . The counter electrodes were Pb/PbSO_4 in the sulfate solution and Ag/AgCl in the chlorides. All data reported here were obtained under a stationary helium atmosphere.

RESULTS

It was found in the present study that an oxidation front could be propagated under helium with a sulfate electrolyte as well as a chloride. This result contrasted with our previous experience in which ambient oxygen was required to propagate the anodic boundary with the sulfate counter ion but not with the chloride (3). The different

^{*}Pc is the conventional symbol for the phthalocyaninato group $\text{C}_{32}\text{H}_{16}\text{N}_8$.



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behavior observed here probably was due to deposition of the dye film on the heated substrate (4). The film resistance again increased under a flowing gas atmosphere, confirming that some water, or solvent, was needed to facilitate the transport of ions through the reacted film.

Merging of the reddish anodic product region with the blue cathodic one was accomplished in several of the dual-boundary experiments. The total resistance, determined from the ratio of the applied voltage to the current, leveled off as the boundaries merged but showed no major change in magnitude. Those data were not amenable to detailed interpretation because the blue/green boundary tended to propagate unevenly.

Reversal of the current in either type of experiment caused a much more pronounced effect, which is illustrated by the voltage-time plot in Fig. 1 and further noted for Na_2SO_4 and KCl electrolytes in Table I. The cell resistance began to drop immediately on reversal of the current and, in several minutes, reached a fairly steady value some 5 to 20 times lower than the resistance measured in the opposite direction before the reversal. In the case of a single boundary, the charge that accompanied this resistance drop was about 5 percent of the original charge required to convert the film. Somewhat greater relative charges were associated with such resistance drops in the dual cells where the boundaries had already begun to merge before the current was reversed. In dual cells containing HCl , the resistance drop was more abrupt than in those with the salt solutions, and no gradual approach to a plateau was evident. The cathodic product with



HCl was dark blue, corresponding to at least a 3-electron reduction from the green state (5).

Prolonged reverse electrolysis in a single-boundary cell led to generation of a new color front at the solution interface. For example, with Na_2SO_4 , a light blue phase began to appear at the electrolyte interface in a previously oxidized film after the resistance drop was completed. Some general fading of the reddish film toward green had occurred by that time, but no bright green band appeared near the metal contact. Finally, the measured resistance increased gradually as the blue phase was propagated.

DISCUSSION

The rapid drop of resistance on current reversal probably signalled the onset of electronic conduction through mixed oxidation states in the dye. Apparently, there remained sufficient continuity of the organic structure to support this type of conduction, even after the film was swollen by the counter ions and solvent. With neutral electrolytes, electron exchange between LuPc_2^+ and LuPc_2 or between LuPc_2^- and LuPc_2 can be envisioned, respectively, for an oxidized or reduced film. Protonated forms, including LuHPc_2 , would be expected to participate in a film converted with an acidic electrolyte (5).

To understand the effect of current reversal more fully, one may consider the example of an oxidized film, consisting of the anion



conductor $\text{LuPc}_2^+\text{Cl}^-$, in contact with a KCl solution. When a cathodic current is applied, LuPc_2 begins to form, an equivalent amount of Cl^- returns to the solution, and the electronic conductivity increases. Initially, this may enhance the mobility of the chloride ion (6), but a phase too rich in LuPc_2 would be expected to restrict the passage of ions.

As electrons become available at the solution interface, another reaction path develops: The reduction can proceed one step further to the light blue LuPc_2^- , with the uptake of K^+ from the solution. This light blue phase is a cation conductor which offers no apparent means for anion transport. Once it attains a sufficient thickness, the blue region blocks the further escape of chloride ions to the solution. Conversion of the remaining film to blue can still occur, however, provided the by-product KCl can be accommodated within the film.

This type of mechanism is suggested to explain the behavior of the system at the relatively high current densities used in the current-reversal experiments--typically 15 to 60 mA/cm^2 through the cross section of the dye film. At the much lower current densities commonly encountered in cyclic voltammetry, formation of the green stage may be more clearly resolved; diffusion in the solid, rather than migration, may become a controlling factor; and the foregoing discussion may not be applicable. At the high currents used to switch diphthalocyanine electrochromic displays, however, the type of process represented by this example can be important. In fact, we have used a



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similar two-layer model to account quantitatively for the galvanostatic transient behavior of a cycled lutetium diphthalocyanine film (7).

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TABLE I. EFFECTS OF CURRENT REVERSAL ON FILM RESISTANCES

Electrolyte	^a A _{max}	Film Width (cm)	Film ^b Thickness (μm)	Current (μA)	Total Resistance (ohms) x 10 ⁻⁷		
					Before Reversal	After Reversal (min)	
						0.03	5 15
1M Na ₂ SO ₄	1.7	0.63	0.160	0.15	18c	10	4.0 2.5
1M Na ₂ SO ₄	0.98	1.26	0.093	0.5	27d	7	1.4 1.5
1M KCl	0.89	1.26	0.084	0.7	4.7e	2.6	0.95 0.75

^aOptical absorbance of initial green film at 665 nm.

^bEstimated for a nonporous initial green film (1).

^cSingle-boundary experiment; fully oxidized before reversal.

^dDual-boundary, merged at one edge.

^eDual-boundary, merged in three places.



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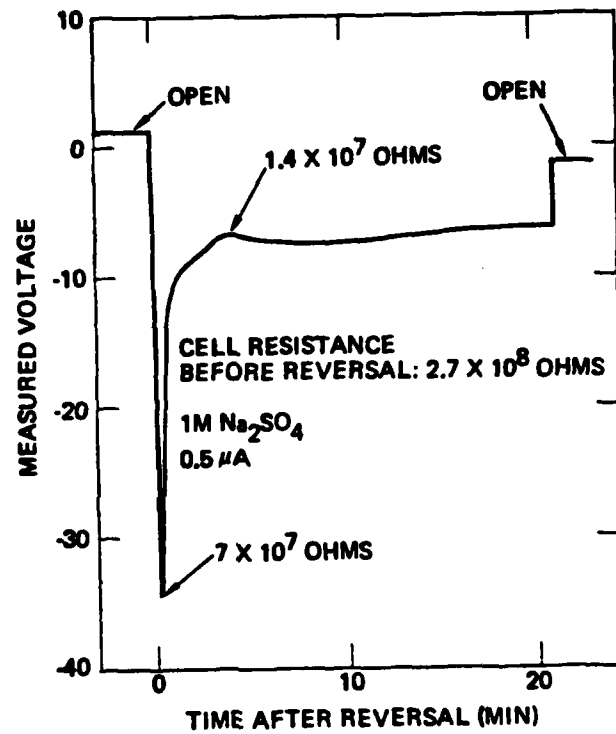
ILLUSTRATION

- 1. Voltage-Time Relationship Following Current Reversal in a
Dual-Boundary Pre-Oxidized Lutetium Diphthalocyanine Film.
Voltage Before Reversal is Given a Positive Sign.**



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